

Claims:

1. A proton-conducting polymer membrane which is based on sulfonated polyazoles and is obtainable by a process comprising the steps
 - A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in a polyphosphoric acid/sulfonating agent mixture to form a solution and/or dispersion,
 - B) application of a layer using the mixture from step A) to a support or an electrode,
 - C) heating of the sheet-like structure/layer obtainable according to step B) under inert gas at temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,
 - D) treatment of the membrane formed in step C).
2. The membrane as claimed in claim 1, characterized in that aromatic tetraamino compounds used are 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, bis(3,4-diaminophenyl) sulfone, bis(3,4-diaminophenyl) ether, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyldimethylmethane.
3. The membrane as claimed in claim 1, characterized in that aromatic dicarboxylic acids used are isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-dicarboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-

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carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or acid chlorides.

4. The membrane as claimed in claim 1, characterized in that aromatic carboxylic acids used are tricarboxylic acids, tetracarboxylic acids or their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably 1,3,5-benzenetricarboxylic acid (trimesic acid); 1,2,4-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid and/or 2,4,6-pyridinetricarboxylic acid.

5. The membrane as claimed in claim 1, characterized in that aromatic carboxylic acids used are tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably benzene-1,2,4,5-tetracarboxylic acid; naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid; benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid.

6. The membrane as claimed in claim 4, characterized in that the content of tricarboxylic acids or tetracarboxylic acids (based on dicarboxylic acids used) is from 0 to 30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%.

7. The membrane as claimed in claim 1, characterized in that heteroaromatic carboxylic acids used are heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids in which at least one nitrogen, oxygen, sulfur or phosphorus atom is present in the aromatic, preferably pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and also their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or their acid chlorides.

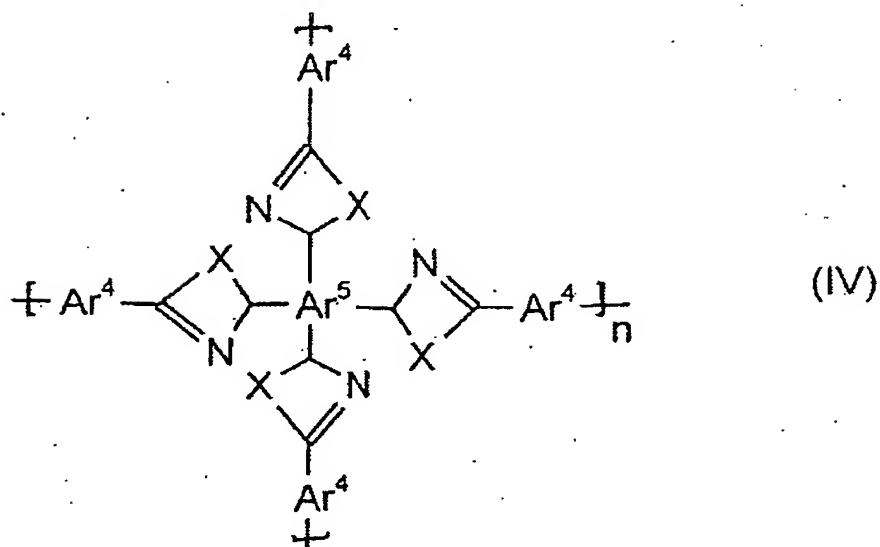
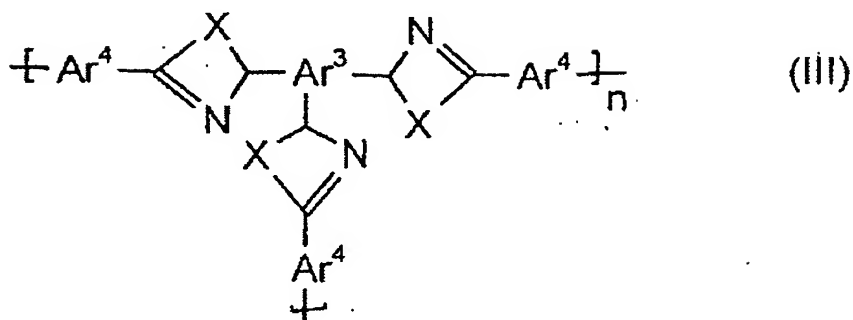
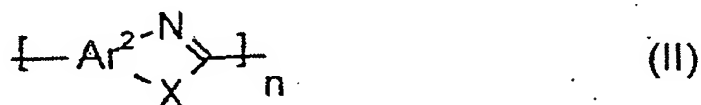
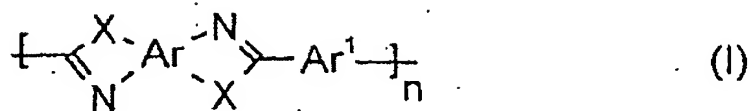
8. The membrane as claimed in claim 1, characterized in that the sulfonating agent used in step A) is selected from the group consisting of i) concentrated

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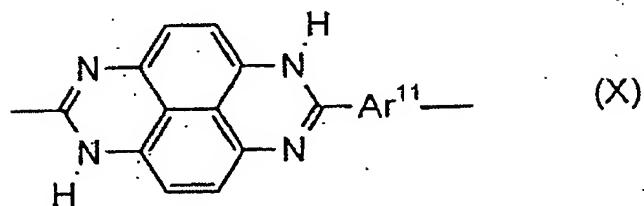
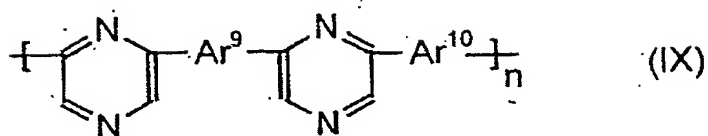
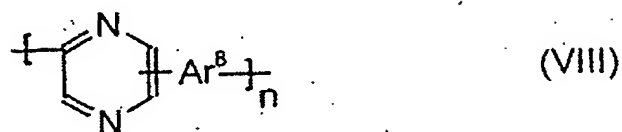
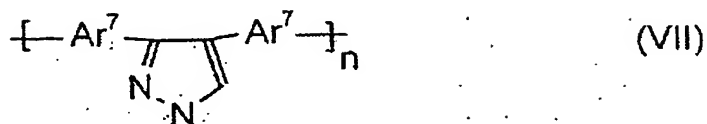
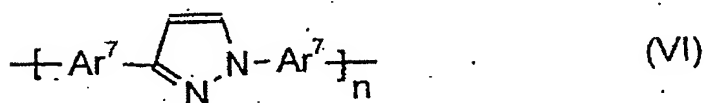
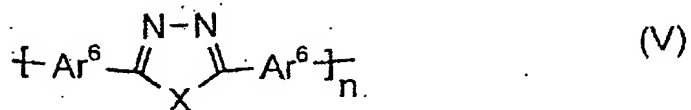
sulfuric acid (>95%), ii) chlorosulfonic acid, iii) a complex of SO₃ with a Lewis base or other organic constituents, iv) an acyl or alkyl sulfate, v) an organic sulfonic acid and vi) mixtures of i to v.

- 5 9. The membrane as claimed in claim 1, characterized in that aromatic and heteroaromatic diaminocarboxylic acids used are diaminobenzoic acid and its monohydrochloride and dihydrochloride derivatives.
- 10 10. The membrane as claimed in claim 1, characterized in that a polyphosphoric acid having an assay calculated as P₂O₅ (acidimetric) of at least 83% is used in step A).
- 15 11. The membrane as claimed in claim 1, characterized in that a polymer which comprises recurring azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII)

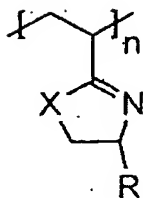
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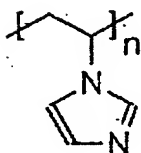
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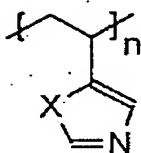
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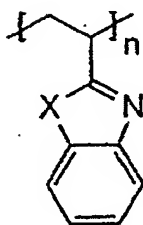
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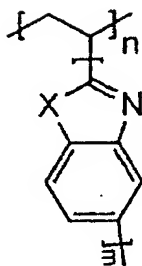
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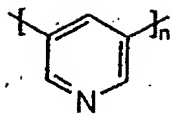


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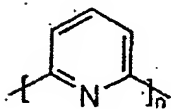


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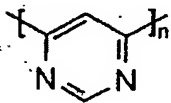
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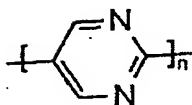
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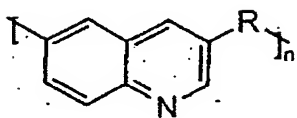
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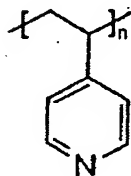
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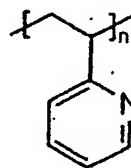
(XIX)



(XX)



(XXI)



(XXII)

where

the radicals Ar are identical or different and are each a tetravalent

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aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar¹ are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar² are identical or different and are each a divalent or trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar³ are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar⁴ are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar⁵ are identical or different and are each a tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar⁶ are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar⁷ are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar⁸ are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar⁹ are identical or different and are each a divalent or trivalent or tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar¹⁰ are identical or different and are each a divalent or trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar¹¹ are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals X are identical or different and are each oxygen, sulfur or an amino group which bears a hydrogen atom, a group having 1-20 carbon atoms,

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preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical, the radicals R are identical or different and are each hydrogen, an alkyl group or an aromatic group and
5 n, m are each an integer greater than or equal to 10, preferably greater than or equal to 100, and has a sulfur content of from 2 to 20% by weight (determined by means of elemental analysis), is formed in step C).

- 10 12. The membrane as claimed in claim 1, characterized in that the viscosity is adjusted by addition of phosphoric acid after step A) and before step B).
13. The membrane as claimed in claim 1, characterized in that the membrane produced according to step C) is treated in the presence of moisture at
15 temperatures and for a time until the membrane is self-supporting and can be detached from the support without damage.
14. The membrane as claimed in claim 1, characterized in that the treatment of the membrane in step D) is carried out at temperatures from above 0°C to
20 150°C, preferably at temperatures in the range from 10°C to 120°C, in particular from room temperature (20°C) to 90°C, in the presence of moisture or water and/or steam.
15. The membrane as claimed in claim 1, characterized in that an electrode is selected as support in step B) and the treatment according to step D) is such
25 that the membrane formed is no longer self-supporting.
16. An electrode provided with a proton-conducting polymer coating which is based on polyazoles and is obtainable by a process comprising the steps
30 A) mixing of one or more aromatic tetraamino compounds with one or more aromatic sulfocarboxylic acids or esters thereof which contain at least two carboxylic acid groups and one sulfonic acid group per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic sulfonated diaminocarboxylic acids, in a polyphosphoric acid to form a
35 solution and/or dispersion,
B) application of a layer using the mixture from step A) to an electrode,
C) heating of the sheet-like structure/layer obtainable according to step B) under inert gas at temperatures of up to 350°C, preferably up to 280°C, to

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form the polyazole polymer,

D) treatment of the membrane formed in step C).

- 5
17. A membrane-electrode unit comprising at least one electrode and at least one membrane as claimed in one or more of claims 1 to 15.
18. A membrane-electrode unit comprising at least one electrode as claimed in claim 17 and at least one membrane as claimed in one or more of claims 1 to 15.
- 10
19. A fuel cell comprising one or more membrane-electrode units as claimed in claim 17 or 18.

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